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Determination and Characterization of Photocatalytic Products of Linear Alkyl Sulphonate by High Performance Liquid Chromatography and Nuclear Magnetic Resonance

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Abstract

In this study, Linear Alkyl Sulfonate (LAS) as anionic detergent active compounds was treated with photocatalytic method. The method degrades LAS to form CO_2 and H_2O. Time variations performed to the photocatalysis was conducted hour to hour, from 1 to 5 hours. Determination of LAS concentration was carried out using methylene blue active substances (MBAs), whereas characterization of LAS structure was observed using high performance liquid chromatography (HPLC) and nuclear magnetic resonance spectrometry (NMR). The results showed that 69.9% of LAS decomposes 65.1% of CO_2 are formed.

Keywords: Catalysis, Carbon dioxide (CO_2), Degradation, Linear Alkyl Sulfonate (LAS).

1. Introduction

Linear Alkyl Sulfonate (LAS) are anionic surfactants as anionic detergent active compounds. Detergent waste waters generated from industrial and household waste used for washing purposes[1]. The presence of excess detergent waters is very dangerous for the environment because it is a carcinogen, causing odor and lead to the uncontrolled growth of water hyacinth and cause silting of rivers. Biodegradation of natural detergents have been studied with bacteria *Pseudomonas pseudoalcaligenes, Alcaligenes paradoxus,*[2]. In addition to the study with *Pseudomonas aeruginosa* W51D*, Nitrosomonas* and *Nitrosospira Strains, Bacillus laterosporus* and *Pseudomonas aeruginosa,* adsorption with activated sludge process[3]. Furthermore there was also study about method of flocculation, flotation, adsorption, activated carbon[4].

Processing with adsorption, flocculation, coagulation and advanced oxidation methods produces unwanted sludge, biological treatment for refractory compounds which are difficult to degrade ineffectively. Therefore, the recommended method of treatment is through advanced oxidation processes AOPs (Advanced Oxidation Processes) as the process fast and safe, detergent degradation by this method has also been developed a lot of them, the LAS degradation by photolysis methods, photocatalytic, photophenton and ozonation[5], an anionic surfactant degradation by ozonation method and or UV radiation, surfactant degradation by hydroxyl radicals from photo-phenton catalyst iron hydroxion complex compounds (III)[4].

Photocatalytic process can be defined as the process of chemical reactions assisted by light and catalyst. Therefore, due to the use of light and a solid catalyst, it is called heterogeneous photocatalyst. Reactions that occur

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in this process involves an electron-hole pair (e and h^+, the positive hole-electron) on the surface of the semiconductor material. Based on this definition, it can be explained that some of the steps photocatalyst is an oxidation-reduction reaction involving e and h^+ pairs. Photocatalyst phenomenon on semiconductor surfaces described in Figure 1.

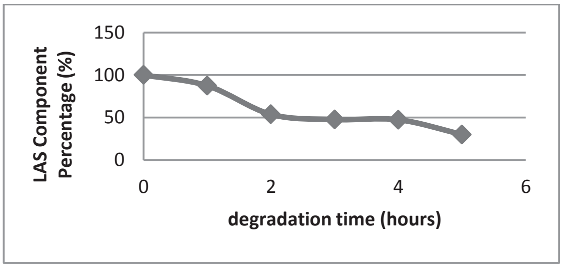

Fig. 1. The relationship between time photocatalyst with LAS percentage remaining components

If an n-type semiconductor exposed to light (*hv*) with corresponding energies, then e in the valence band will move to the conduction band, and left h^+ in the valence band. Most of the e- and h^+ pairs will recombine again, either on the surface (line A) or in the bulk particles (line B), while the some couples e and h^+ can survive until the surface of the semiconductor (lanes C and D), where h^+ can initiate oxidation reactions and on the other hand e will initiate a chemical reduction reaction that is around the surface of the semiconductor. The composition of the photocatalytic reactor diverse. The optical path of light in the rector is made is the choice for photoreactor geometry. This relates to the determination of how much radiation is adsorbed by the reaction suspension, thus determining the efficiency of the photocatalytic process[1],[6].

LAS that has been in the photocatalyst is converted into carbon dioxide (CO_2) and H_2O (Hidaka et al., 2004; Horváth and Huszánk, 2003) and in general the CO_2 can be determined by several methods such as non-dispersive infrared absorption spectrometry, thermal conductivity, gravimetry, titration (volumetric), and various methods of chromatography, and conduktometry[7].

2. Materials and Methods

Determination of detergent levels of degradation has been analyzed based on the content of LAS as the active compound. The standard method is the method of Methylene Blue Active Substances (MBAs) using a spectrophotometer measuring instrument[3,8,9]. LAS structure has been identified by high performance liquid chromatography[4], GC-MS method[10], the GC method in comparison with spectrophotometry and a combination of liquid chromatography and ion chromatography.

2.1. Materials

The chemicals used were TiO_2 powder (Merck Lab.), Silica gel 60 (0,040- 0.063 mm), TiO_2 Degussa P 25, distilled water, membrane filters 0.45 mm, aqua demineralized, chloroform ($CHCl_3$), anhydrous sodium sulfate (Na_2SO_4), linear alkyl sulphonate (LAS), phenolftalein, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) of concentrated, reagent methylene blue, granular sodium phosphate hydrate ($Na_3(PO_4)_2$, sodium hydrogen phosphate hydrate ($NaH_2PO_4.H_2O$), methanol (CH_3OH), hydrogen peroxide (H_2O_2) 30%, glass wool, D_2O, Acetonitril $(ACN)_{(l)}$, aquabides, Methanol (CH_3OH).

2.2. Photocatalytic Method

The equipment used was a UV-Visible spectrophotometer, pH meter ORION 420A models. In addition it is also used filter photometer, 500 mL separating funnel, photocatalytic reactor (tube, lamp UV-A Blacklight Blue Bulbs), organic compound degradation analyzer (CO_2 sensor), NMR, HPLC and other glassware used in the laboratory.

The design of photocatalytic reactor, photocatalytic reactor made with a batch system. The tube is made of pyrex. Black light UV lamp 125 Watts used as its photon beam, placed over the tube. Irradiation process is done in a closed system (enclosed metal container equipped with a blower and stirer). Tubular photocatalytic reactor, was made[6,9]. In addition, also available on the design of reactors[1,11].

Standard operating conditions: The conditions used in the assay reactions were performed without pH control. The concentration of catalyst used in the performance test reactor is 1 g/L. Testing is done by varying the length of time photocatalyst, hour-1, 2, 3, 4, and 5. Analyte testing is also done before the process.

2.3. Analysis of The Formation of CO_2

Analysis performed by bubbling carbon dioxide (CO_2) produced to the solution of 100 mL of 1 M NaOH. NaOH does not react with CO_2 titrated with 1M HCl using phenolphthalein indicator.

2.4. LAS Content Analysis

The analyzes were performed by using methylene blue active substances (MBAs) in the LAS standard of 100 mg/L. Absorbance measurements performed at a wavelength of 652 nm to $CHCl_3$ as a blank. LAS structural analysis by NMR, Standard LAS before and after degradation dried and then dissolved in D_2O, each specified number of neighboring hydrogen atoms (^{1}H-NMR) and the number of carbon atoms (^{13}C-NMR). LAS structure analysis by HPLC: LAS standards before and after degradation dried and dissolved in Acetonitril, water (40:60), sampled as many as 20 µL, injected on a C_{18} column and flowing solvent with a flow rate of 0.5 mL/min, the presence of compounds detected by UV-Vis detector at a wavelength of 210 nm.

3. Results and Discussion

In the photocatalytic process will form electron-hole pairs that occur at the time of the semiconductor TiO_2 subject to light. Hole formed will adsorb organic molecules found on the surface of the catalyst, to form OH radicals. In the process of the photocatalytic degradation of LAS, mechanisms involved are LAS molecules adsorbed on the catalyst surface, OH radicals formed later. In the structure of LAS can be assumed that the OH radicals will attack the LAS structure forming intermediates, then mineralized to form CO_2 and H_2O[2,12], with the following reaction:

$$C_cH_hO_o + [(h\text{-}2o) / 4 + n]\ O_2 \rightarrow TiO_2, hv \rightarrow cCO_2 + h / 2\ H_2O$$

Quantitative determination of CO_2 produced is equivalent to the content of organic substances in the sample, in this study the amount of CO_2 that is formed is equivalent to the content of LAS.

3.1. Quantitative determination of CO_2 by Titration Method

Analysis of LAS concentration and CO_2 formation during the photocatalytic process is shown in Fig. 1 and Fig. 2, seen that LAS significantly degraded after degradation at the 1st, and in the next hours degradation continues until the 5th of 69.9%. This is possible because the photocatalytic process will be formed OH radicals, which will oxidize compounds LAS, so that quantitative LAS concentration decreased, which means that the longer the degradation process, LAS concentration decreases due to degradation (Figure 1). LAS degraded completely starting at 1 and form CO_2 gas which continues to grow in the next hours to 65.1% (Figure 2). It is seen that the formation of CO_2 is significant with decreasing concentration of Linear Alkyl Sulfonate components.

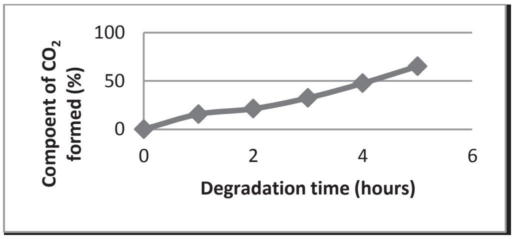

Fig. 2. The relationship between photocatalytic time with percentage of CO_2 formed components

Determinations were performed by bubbling carbon dioxide (CO_2) produced in 100 mL of 0.01M NaOH. NaOH solution which does not react with CO_2 and then titrated with 0.01M HCl using phenolphthalein indicator. At the same Erlenmeyer, dissolved CO_2 is titrated with 0.01 M HCl using methyl orange indicator.
The reaction is as follows:

OH (excess) + $H^+ \rightarrow H_2O$
$HCO^- + H^+ \rightarrow H_2CO_3$
Titrant Volume (HCl) required is recorded as V_1 = mL
$HCO_3 + H^+ \rightarrow H_2CO_3$
Titrant Volume (HCl) required is recorded as V_2 = mL
H_2CO_3 $H_2O + CO_2$
$V_1 - V_2$ = concentration of OH^-
V_2 ekivalent with HCO_3 concentration and ekivalent with CO_2 concentration.

3.2. Determination by Nuclear Magnetic Resonance / NMR

LAS structure determination of degradation products analyzed by NMR, the results shown in Figure 3 and Figure 4.

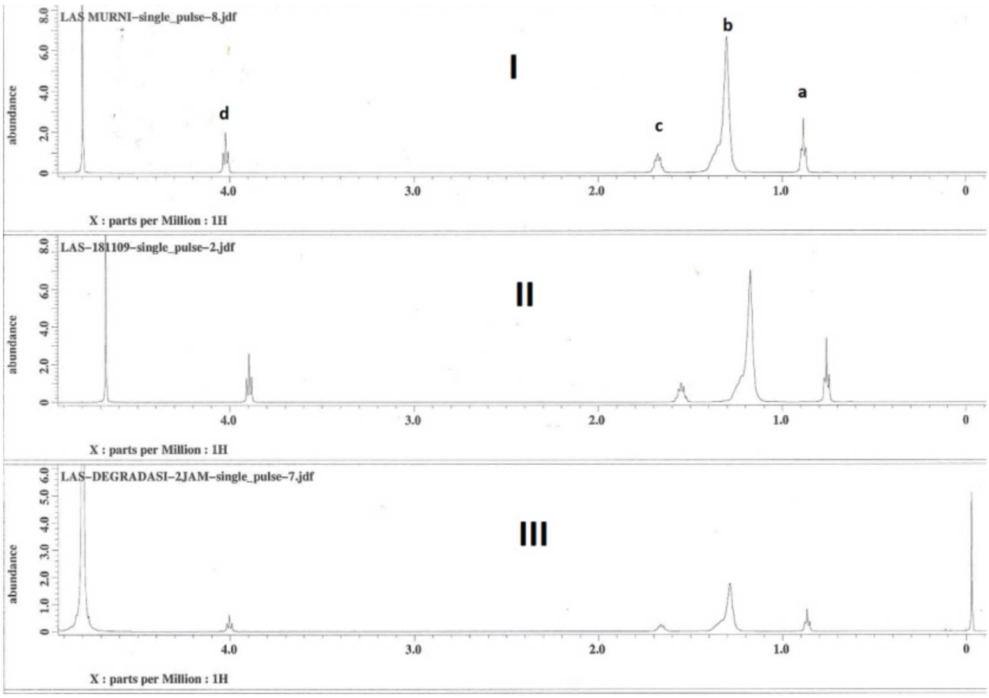

Fig. 3. [1]H-NMR spectrum of Linear Alkyl Sulfonate (LAS) before degradation (I) and after degradation (II and III).
All spectra display the same sequence of resonance signal.

Proton in the aliphatic chain resonance below 2 ppm where three signal are present. The signal at 0.9 ppm is attributable proton of $H_3C – CH_3$. The signal at 1.3 and 1.6 ppm are attributable proton of the CH_2 groups bonded to the carboxylic groups. Finally the signal at 4.1 ppm is attributable to the proton of the $CH_2 – O – S$[13].

The regular structure give the following resonances (Hummel, 2000).
$CH_3 – (Ch_2\text{-}CH_2)n – CH_2 –O\text{-}S$
a b and c d

The chemical shifts (δ) for various structure are given below:

δ (ppm)	Structure
0.8 – 0.9	$H_3C – CH_3$
1.3	$CH_2 – CH_2 – CH_2$
4.1	$CH_2 – O – S$

From the [1]H-NMR (Figure 4) showed a decrease in the concentration of LAS, although the shape and structure of the group is still bound. NMR analysis results showed that the photocatalytic process, LAS degraded, and it is degraded directly form CO_2, while the rest of the LAS is not degraded remains in the form of the original structure.

Analysis of the structure of the Nuclear Magnetic Resonance / NMR, [13]C-NMR (Figure 4) shows that there is no change in the structure of Linear Alkyl Sulfonate before and after degradation means the number of carbon atoms contained in the sample component is fixed.

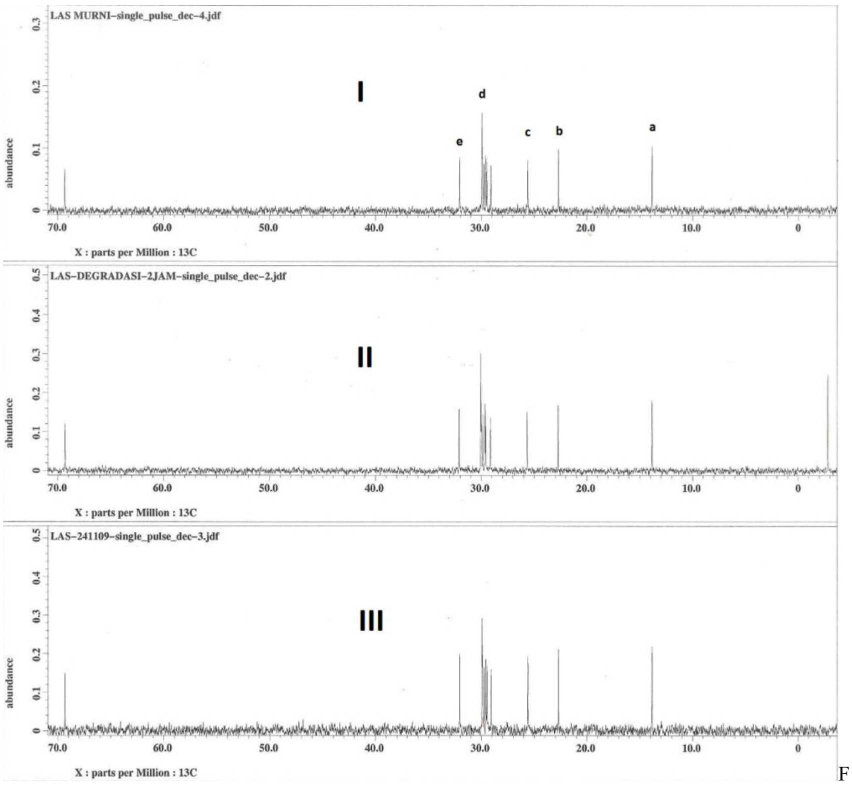

Fig. 4. ^{13}C-NMR spectrum of Linear Alkyl Sulfonate (LAS) before degradation (I) and after degradation (II and III)

Figure 4. shows broad-decoupled ^{13}C-NMR of a linear alkyl sulfonate. The signal at 13.0 ppm (a) is attributable structure of CH_3. The signal at 22.0 (b) and 25.0 ppm (c) are attributable structure of CH_2. Finally the signal at 30.0 (d) and 32.0 ppm (e) is attributable structure of the CH_2, quarternary aliphatic C[13].

The following table shows the assignment of the signals to surfactant structure[14].

Signal, δ (ppm)	Structure
9 – 30	CH_3, CH
24 – 40	CH_2
30 – 50	CH_2, quarternary aliphatic C

3.3. Determination by High Performance Liquid Chromatography (HPLC)

Intermediates are formed also analyzed using a High Performance Liquid Chromatography (HPLC) and the result is as shown in Figure 5.

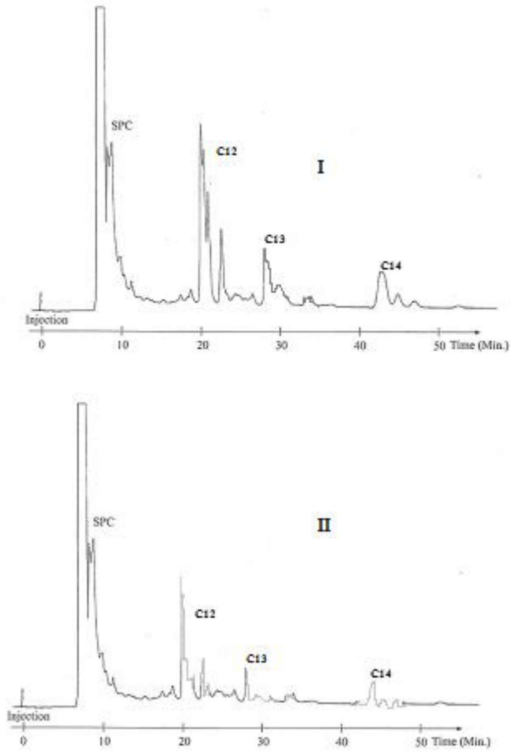

Fig. 5. High Performance Liquid Chromatography spectrum of Linear Alkyl Sulfonate (LAS) before degradation (I) and after degradation (II)

Spectrum above (Figure 5) shows that there is no change to the structure of LAS compounds before and after degradation, but from the calculation area obtained a decrease which means that the components LAS concentration decreased. From the results of spectrophotometric analysis, NMR and HPLC provide information that the LAS with photocatalytic process for 5 hours with a reactor design that was made, partially degraded components forming CO_2 perfect start to the hour-1 and others remain in its original structure. Generally when organic compounds degraded, will form intermediates such as alcohols, carboxylic acids, aldehydes and peroxides, but because the presence of these compounds very quickly it was not detected by the analyser used.

Based on the information obtained it can be proposed reaction mechanism that occurs in the process of photocatalytic Linear Alkyl Sulfonate compounds are as shown in Figure 6.

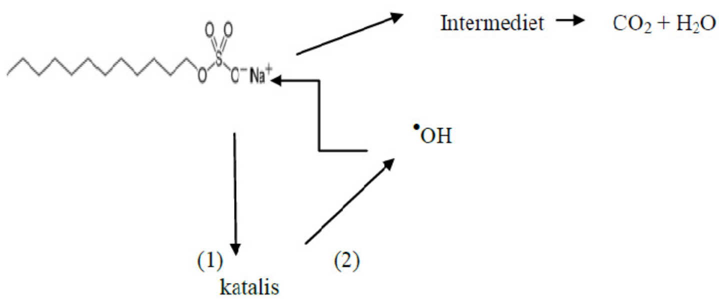

Fig. 6. Proposed mechanism of photocatalytic reaction of linear alkyl sulphonate (LAS)

Conclusion

Photocatalytic process to Linear Alkyl Sulfonate (LAS) with a slurry reactor working in batches using Degussa P25 TiO_2 catalyst within 5 hours, have successfully degrade LAS amounted to 69.9%. The mechanism of the degradation reaction is partially degraded components perfectly formed CO_2 within 5 hours up to 65.1% and the other part remains in its original structure.

Acknowledgements

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